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Photometric Determination of Thorium in the Soil

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PHOTOMETRIC DETERMINATION OF THORIUM IN THE SOIL

[Fotometricheskoye opredeleniye toriya v pochve]

by

B. I. Zhukov
Agriculture Scientific Research Institute,
Ministry of Agriculture, USSR

Pochvovedenie, 2: 156-158, Feb. 1971

A method is described for the photometric determination of thorium in soils. This involves decomposition of the sample by sintering with sodium peroxide, and precipitation on calcium oxalate. Sensitivity of the proposed method is 0.04 µg/ml. This permits determination of down to $1 \cdot 10^{-6}$ g/g of soil. The analysis is performed without platinum vessels or hydrofluoric acid.

For study of the migration and transport of thorium with a plant crop, a sufficiently simple and sensitive method of determination of its content in the soil is necessary. The majority of existing methods are based on determination of thorium in rocks [12, 7, 8, 3, 2, 13]. Part of the methods are complicated, since they were developed for materials with a high (with respect to thorium) uranium content [11, 5]. The methods which can be used for determination of thorium in soils do not ensure

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A method of photometric determination of thorium in soils (with arsenaso III), after decomposition of the sample by sintering with sodium peroxide and precipitation on calcium oxalate is described. Sensitivity of the proposed method is 0.04 μg/ml. This permits determination of down to $1 \cdot 10^{-6}$ g/g of soil. The analysis is performed without platinum vessels or hydrofluoric acid.

For study of the migration and transport of thorium with a plant crop, a sufficiently simple and sensitive method of determination of its content in the soil is necessary. The majority of existing methods are based on determination of thorium in rocks [12, 7, 8, 3, 2, 13]. Part of the methods are complicated, since they were developed for materials with a high (with respect to thorium) uranium content [11, 5]. The methods which can be used for determination of thorium in soils do not ensure

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sufficiently reliable results to be obtained, with a high content of Mn, Fe, Zr, Ti [6, 1], or they are laborious.

The method we have developed is based on the content of thorium in calcium oxalate and subsequent photometric determination of thorium with arsenaso III.

In preparation of soils for analysis, three methods were tested: fusion of the soil with sodium peroxide, with a mixture of caustic potash and soda and decomposition of the sample with hydrofluoric acid.

Direct determination of thorium after alkaline fusion of the soil, without elimination of impurities, leads to overstated results. Elimination of interfering elements from the solution was carried out in a column with AV-17 resin and by means of co-precipitation of thorium with calcium.

According to the data of Nabivanets and Kudritskaya [9], with a concentration of HCl $\geq$ 9, uranium, in the form of the $[UO_2Cl_4]^{''}$ ion, is absorbed by the AV-17 resin, and thorium, because of the low stability of the compound $[ThCl_5]^{'}$ is not retained in the column. The sample, dissolved in 4 N HCl, was passed through a column with an anion-exchange resin. Evidently, the interference was caused by the presence, not of uranium, but of other elements, since the thorium content did not change after purification of the solution on AV-17 resin.

Co-precipitation of thorium on calcium oxalate has been used by a number of investigators, for separation of thorium from the interfering elements [10, 8]. Data which we obtained indicate that, after oxalate co-precipitation of thorium on calcium, the results do not differ practically from the data obtained by the method using hydrofluoric acid.

TABLE 1
OPTICAL DENSITY OF BACKGROUND SOLUTION vs. CALCIUM CONCENTRATION

a Содержание кальция, мг/10 мл	b Оптическая плотность
800	0,08
1600	0,11
3200	0,15

Key: a Calcium Content, mg/10 ml
b Optical Density

[Translator's Note: commas in tabulated figures are equivalent to decimal points.]

In connection with the fact that calcium was used as the carrier, the effect of the concentration of this element on the color intensity of the solution was tested (Table 1).

Thus, the calcium content in the sample must be taken into account in the analysis, and the corresponding amount of it must be introduced in the background solution.

Analysis

A 0.5 g soil sample, sifted through a sieve with 0.25 mm openings, is sintered in a porcelain crucible at 400-450°, with 6 times the amount of sodium peroxide. After cooling the crucible, it is placed in a 400 ml beaker, 250-300 ml of distilled water is added and it is heated to boiling. After standing for a period of 15 min, the precipitate is filtered off, washed with hot water and dissolved in 8-10 ml of 4 N HCl in a 300 ml beaker. The resulting solution is neutralized with ammonia, until the start of precipitation of the hydroxide, and 4 ml of calcium chloride (concentration 100 mg/ml Ca) and 5 drops of H_2O_2 are added, it is diluted with water to 150 ml and boiled for 5 min. Then, 6 g of oxalic acid is

introduced, and it is left to settle for 10-12 hours. The precipitate is filtered off through a "blue-stripe" filter and washed with a 1% oxalic solution. The filter and precipitate are dried in a drying oven and calcined at 600-650°. The calcined residue is dissolved, by heating in a minimum quantity of 4 N HCl (in 10-15 ml), and it is filtered into a 25 ml volumetric flask. 0.16 g of oxalic acid, to mask zirconium, 40 mg of ascorbic acid, to reduce trivalent iron are added to the flask, and 4 N HCl is added up to the mark. 10 ml of the prepared solution is transferred to a small beaker, 0.2 ml of 0.2% arsenaso III solution is added, and it is measured in a FEK-57 photometer with red filter, in a cuvette ℓ = 10 ml. The 4 N HCl solution, to 25 ml of which 0.16 g of oxalic acid, 40 mg of ascorbic acid and 400 mg of calcium also are added, is used as the background. Before photometry, 0.2 ml of 0.2% arsenaso III solution is added to 10 ml of this solution.

In plotting the calibration curve, standard thorium chloride solutions are used, to which the same reagents are added as to the test solutions. The thorium content in a 25 ml volume of the standard solution in a flask, is from 1 to 15 μg.

The thorium content in different types of soils was determined by the method described above (Table 2). For comparison, thorium was determined in the same samples, by the method of Savvin et al. [12], which includes decomposition of the soil with hydrofluoric acid.

The convergence of the results of the analyses performed by the two methods is completely satisfactory. The sensitivity of the proposed method is 0.04 μg/ml. This permits determination of down to 1.10^{-6} g of thorium in 1 g of soil.

TABLE 2

THORIUM CONTENT IN VARIOUS TYPES OF SOIL

a Почва	b Содержание тория, %		e Разница, %
	c осаждением на оксалате	d разрушение пробы HF	
f Серозем обыкновенный	$16 \cdot 10^{-4}$	$17 \cdot 10^{-4}$	−6,0
g Серо-бурая	$13,04 \cdot 10^{-4}$	$13 \cdot 10^{-4}$	+0,3
h Каштановая	$17 \cdot 10^{-4}$	$15 \cdot 10^{-4}$	+13,0
i Горный черозем	$11 \cdot 10^{-4}$	$10,3 \cdot 10^{-4}$	+6,8
j То же	$12,1 \cdot 10^{-4}$	$12,8 \cdot 10^{-4}$	−5,4

Key: a Soil
b Thorium content, %
c Co-precipitation on Oxalate
d HF Decomposition of Sample
e Difference, %
f Common grey desert soil
g Brownish-grey
h Chestnut
i Mountain chernozem
j Same

Performance of the analysis does not require platinum vessels or hydrofluoric acid.

REFERENCES

1. Baranov, V. I. and L. A. Kuz'mina, "Ionic method of determination of age of marine sediments," DAN SSSR 97 (1954).

2. Vladimirova, V. M. and N. K. Davidovich, "Colorimetric determination of thorium with arsenaso III in niobium-containing products," Zavodskaya laboratoriya 26 (1960).

3. Volynets, M. P., "Brief report," ibid.

4. Grodzenskiy, D. M., Yestestvennaya radioaktivnost' rasteniy i pochv [Natural Radioactivity of Plants and Soils], "Naukova dumka" Press, Kiev, 1965.

5. Karalova, Z. K. and Z. I. Pyzhova, "Ion-exchange concentration of thorium isotopes, with simultaneous separation from uranium," Zhurnal analiticheskoy khimii 23 (1968).

6. Kuz'mina, L. I., "Determination of uranium, thorium and ionium in marine sediments," ibid. 13/1 (1958).

7. Luk'yanov, V. F., S. B. Savvin and I. V. Nikol'skaya, "Photometric determination of thorium in zircons, with the new reagent arsenaso III," ibid. 25 (1959).

8. Luk'yanov, V. F., I. V. Nikol'skaya and V. S. Kozlova, "Analytical chemistry of thorium," Radiokhimiya 3/2 (1961).

9. Nabivanets, B. N. and L. N. Kudritskaya, "Study of the state of thorium in solutions of perchloric, hydrochloric and nitric acids by electrodialysis and ion-exchange chromatography methods," Ukrainskiy khimicheskiy Zhurnal 30/10 (1964).

10. Paley, P. N., Z. K. Karalova, N. P. Shibeyeva and Z. N. Pyzhova, "Determination of ionium and the sum of thorium isotopes in uranium materials," Zhurnal analiticheskoy khimii 21/1 (1966a).

11. Paley, P. N., Z. K. Karalova, N. P. Shibeyeva and Z. N. Pyzhova, "Separation of ionium ($^{230}_{90}$Th) from uranium, protoactinum, iron, manganese and europium by means of cation exchange," ibid. 21/7 (1966b).

12. Savvin, S. B. and V. V. Bargeyev, "Photometric determination of thorium in rocks with arsenaso III," Zavodskaya laboratoriya 26 (1960).

13. Fruktova, Ye. V., G. Kh. Sadova, V. N. Ivanova and F. V. Zaykovskiy, "Photometric determination of thorium in natural materials by the use of arsenaso III," Zhurnal analiticheskoy khimii 19/1 (1964